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CHEMICAL & ENGINEERING

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CHEMICAL OSCILLATIONS

Patterns in space and time

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CHEMICAL & ENGINEERING NEWS

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MARCH 30, 1987

News of the Week

■ **National Academy of Sciences begins series of seminars on research at forefront of technology, engineering, and science.** **Page 4**

■ **Discovery of first ferromagnetic organic polymers is reported by U.S. and Soviet research groups.** **Page 5**

■ **British Petroleum, already a 55% owner, announces plans to acquire remaining 45% of Standard Oil.** **Page 5**

■ **Strong rise in chemical company stock prices during first three months of 1987 reflects stock market surge.** **Page 5**

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Education

Third World scientists will get advanced training in biotechnology methods in six-week program offered by West German institute. **Page 17**

Technology

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Immunoassay technology for quantitative analysis of organic compounds is being developed by Westinghouse Bio-Analytic Systems. **Page 22**

Books

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Cover: Bull's-eye patterns in petri dish are formed by the oscillating chemical activity of a thin layer of Belousov-Zhabotinskii reactants. Photo by Arthur T. Winfree, University of Arizona

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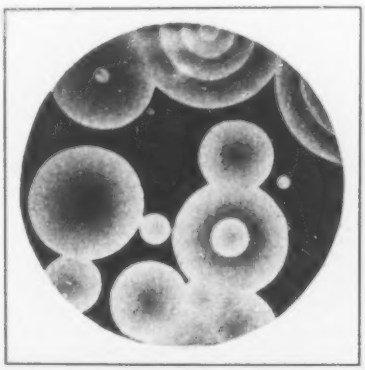


Special Report

Despite both experimental and theoretical evidence for the existence of chemical oscillations in time and space, only recently have they evolved into a major field of chemical research. **Page 24**

First ferromagnetic organic polymers prepared

Two independent research groups in the Soviet Union and U.S. just published accounts of the discovery of the first organic polymers that spontaneously become magnetic at ambient temperatures. This property, known as ferromagnetism, results when the spins of unpaired electrons in a material spontaneously orient themselves in the same direction, creating a bulk magnetic effect.

Ferromagnetism is the last entry on the list of electronic properties that once were thought to be restricted to inorganic materials but have now also been observed in organic materials. That list includes metallic conductors, semiconductors, and superconductors. Organic ferromagnets might one day replace metals or metallic compounds now used for their magnetic properties, such as chromium dioxide, which is used to coat magnetic recording tape.

The Soviet researchers, led by A. A. Ovchinnikov of Moscow's Institute of Chemical Physics, prepared their ferromagnetic material by polymerizing a stable biradical monomer consisting of a cyclic nitroxyl group attached to either end of a diacetylene fragment [*Nature*, **326**, 370 (1987)]. The Soviets apparently were not able to control the degree of polymerization or the size of the polydiacetylene chains thus formed.

In a commentary in the same issue of *Nature*, Richard H. Friend of the University of Cambridge, U.K., points out that "only a small fraction (0.1%) of the monomer prepared by the Soviets is converted to ferromagnetic polymer, although this fraction can be magnetically separated from the residue." The polydiacetylene polymer remains ferromagnetic up to about 150 °C, a limit that Friend calls "respectably high." Above that temperature, the electron spins lose their alignment, leading to a loss of magnetism.

The Soviet work is significant, Friend says, because it shows that the electron spins of polymer-bound radicals can align along the length of the polymer chain. But, he adds, it is "far from ideal," because the yield of ferromagnetic material is so low and the product is so poorly characterized.

The U.S. results, just published in *Synthetic Metals* [**19**, 709 (1987)], suffer from similar drawbacks. They were first announced in December 1984 at a scientific meeting by physicist Jerry B. Torrance of IBM Almaden Research Center in San Jose, Calif., and his coworkers. They have observed ferromagnetic behavior in a polymeric material produced by the reaction of 1,3,5-triaminobenzene with iodine. "The chemistry going on in this reaction is a real mess," Torrance says, and his group has not been able to characterize its material. The yield of ferromagnetic polymer in the reaction also is very small (at most 2%), and the product is "not very reproducible," he notes. Nevertheless, the material—when it is obtained—remains ferromagnetic to high temperatures, until it decomposes near 400 °C.

Both groups have established that their polymer's ferromagnetism is not due to any metallic impurities.

Despite the lack of high-yield, well-characterized products in the Soviet and American work, scientists expect these results "will certainly stimulate further efforts to synthesize other organic ferromagnets."

In related work during the past year or so, Du Pont chemist Joel S. Miller and his coworkers have been able to prepare crystalline, organometallic charge-transfer salts such as decamethylferrocenium tetracyanoethylenide, which show reproducible ferromagnetism. However, unlike the aforementioned polymers, this particular salt, for instance, is a ferromagnet only at temperatures below 4.8 K. □

BP to acquire rest of Standard Oil

British Petroleum announced last week that it will make a tender offer to acquire all of the outstanding shares of Standard Oil Co. that it does not already own. The U.K. firm currently owns 55% of Ohio-based Standard Oil, which ranks 59th among U.S. chemical producers.

BP will offer $70 per share in cash for the remaining 45% of Standard Oil, making the deal worth more than $7 billion. Standard Oil's stock price the day before the announcement was $64⅞ per share. Thus the offer, which BP will make no later than April 1, represents a premium of about 8% for stockholders.

To finance part of the deal, BP is seeking loans for $5 billion in the form of a revolving credit with a four-year term.

The combined firm will emerge as a moderate force in the U.S. chemical industry. BP's chemical sales figures in the U.S. are not available, but its BP North America subsidiary produces a number of polymers and specialty chemicals. Standard Oil's chemical sales in 1986 were $1.1 billion, down 21% from 1985, but its operating earnings from chemicals increased 7.5% to $57 million (excluding an extraordinary charge of $14 million in 1985). □

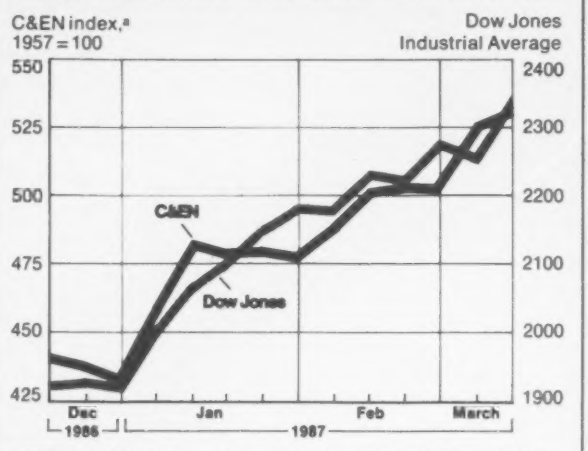
Chemical firms ride stock market surge

For the first three months of 1987, chemical company stock prices have performed just about as stunningly as the widely accepted stock market yardstick, the Dow Jones Industrial Average, which continued setting new records last week.

C&EN's chemical stock index—based on the weighted market value of stocks of American Cyanamid, Dow Chemical, W. R. Grace, Hercules, Monsanto, Rohm & Haas, and Union Carbide—increased 20.6% for the three-month period ending March 20, reaching a level of 532 (1957 = 100). That's essentially the same as the 21% growth in the Dow Jones Industrial Average over the same period, reaching 2333 on March 20. The chemical stock index outperformed the New York Stock Exchange Composite Index, which rose 18.7% during the period, and Standard and Poor's 500, which was up 19.4%.

Generally, however, the indexes of smaller stock activity outperformed the chemical stock index. The best performance was tallied

Chemical stocks reflect heady growth in major industrials over past three months



a C&EN weighted stock price index of American Cyanamid, Dow Chemical, W. R. Grace, Hercules, Monsanto, Rohm & Haas, and Union Carbide.

Chemical stock index keeps pace with most other indexes

	Dec. 19, 1986	March 20, 1987	% change
C&EN Chemical Stock Index	441	532	20.6%
Dow Jones Industrial Average	1928.85	2333.52	21.0
New York Stock Exchange Composite	142.65	169.37	18.7
American Stock Exchange Index	265.46	337.80	27.3
Over-the-Counter Composite	352.24	439.64	24.8
Over-the-Counter Industrials	351.80	462.79	31.5
Standard & Poor's 500	249.73	298.17	19.4
Standard & Poor's 400 Industrials	277.90	341.99	23.1

by the Over-the-Counter Industrials, which rose 31.5%, and the American Stock Exchange Index, which gained 27.3%. The Over-the-Counter Composite increased 24.8% and Standard & Poor's 400 Industrials rose 23.1%.

Growth in C&EN's chemical stock index, good as it has been in the first quarter, still lags that recorded in the most recent annual overview of chemical stock performance in July 1986. At that time, the chemical stock index had posted an annual 47.2% rise to 399 on July 18, compared with the Dow Jones Industrial Average, which rose 30.8% to 1778.

According to Shearson Lehman Brothers vice president and chemical industry analyst Theodore Semegran, recent chemical stock performance has benefited from continued strong chemical business, with particular strength in plastics and organic chemicals. Polypropylene and polyvinyl chloride sales have been particularly strong, he says, resulting in good market performances by three new companies whose stocks were listed on the New York Stock Exchange over the past three months: Aristech (up 63.4% since being issued and closing at $29 per share on March 20), Himont (up 36.8% and closing at $41¾ per share), and Vista (up 89% and closing at $32⅛ per share).

Of the companies in the C&EN chemical stock index, Dow has been the best performer over the past three months, rising 35.2% to $82½ per share on March 20. Next is Union Carbide, gaining 28.8% to close at $29 per share, and American Cyanamid, rising 21% to $97⅜ per share.

The four other companies making up the chemical index had below-average increases, with Grace up 19.1% to $62¼ per share, Rohm & Haas up 18.3% to $43⅝ per share, Hercules up 13.1% to $60½ per share, and Monsanto down 0.3% to $78¼ per share. □

FDA plans to speed up some new drug approvals

After years of debate and controversy, the Food & Drug Administration is about to enter revolutionary new territory in speeding the approval of new drugs aimed at treatment of terminal diseases. The regulations, in effect, would combine the selling and testing of new clinical formulations for patients with life-threatening diseases such as acquired immune deficiency syndrome (AIDS) and cancer.

FDA announced its new proposals, called the "IND Rewrite," in the March 19 issue of the *Federal Register*. The proposals would place on "fast track" the Investigational New Drugs process, allowing physicians to prescribe promising but incompletely tested drugs for terminal diseases. INDs are those drugs for which companies seek FDA approval in order to begin clinical trials. In one sense, FDA scientists would work with industrial researchers as they develop and test the new drugs.

Drug companies haven't come to any consensus about the proposal yet and were meeting last week at the Pharmaceutical Manufacturers Association in Washington, D.C., to develop one. But a major consumer group has long since been up in arms. "These new regulations," says Sidney M. Wolfe, director of the Public Citizen Health Research Group in Washington, "represent a gross decrease in the conditions necessary to distribute these drugs. It is an open invitation for companies to sell drugs that don't have good evidence of safety and efficacy. There are enough charlatans exploiting AIDS patients as it is."

Wolfe says FDA's approval for the sale of azidothymidine (AZT) on March 20 was the model that should be followed. "That was a closed clinical trial," he says. "It involved controlled studies, then distribution. FDA wants to go way beyond this and let these new drugs out loose and jeopardize already sick people." □

Weaker Dollar Hasn't Helped Chemical Trade

That's because much U.S. chemical trade involves countries where the dollar value has remained steady or has grown stronger

The value of the U.S. dollar has fallen dramatically against some major foreign currencies over the past two years. But that drop has not helped the U.S. chemical industry so much as expected.

In fact, the weakening dollar has helped very few U.S. industries, and what help it has provided has been very unevenly distributed among them. That's the conclusion of a study made by Claremont Economics Institute (CEI), Claremont, Calif., on the impact of the declining dollar on various segments of U.S. industry.

CEI president Deborah Allen Olivier says that only a few specific industries will face less international competition as a result of the dollar's depreciation. Fewer still will benefit substantially. Within the chemical and related products sector, only pharmaceuticals will be one of those fortunate few.

Instead, says Olivier, most U.S. producers will actually face tougher foreign competition this year than they did over the past two years, despite the falling value of the dollar. Based on CEI's studies, this could be true for virtually every segment of the chemicals and allied products industry.

The dollar's decline has had a different impact on different industries in the U.S., CEI says, because the major international competition for one U.S. industry may not come from the same region or country as that of another industry. Meanwhile, the dollar has fallen against only a handful of foreign currencies.

The dollar is down primarily against the Japanese yen and the major European currencies. The dollar's decline against those key currencies has attracted a lot of attention and publicity. Conventional wisdom holds that, as a result, the U.S. trade deficit will narrow and industrial production in the U.S. will increase this year.

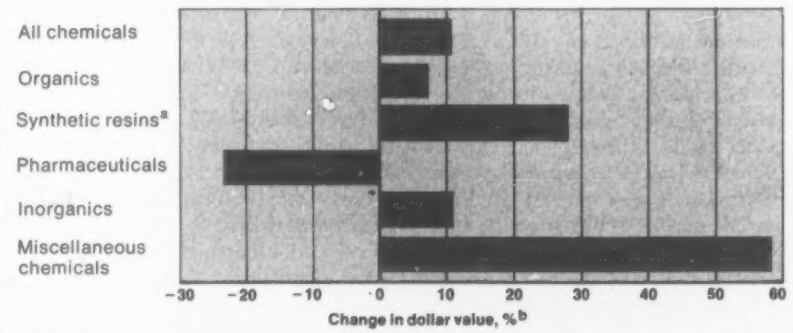
CEI contends that those U.S. producers whose primary rivals are in Japan or Western Europe will, indeed, face less international competition this year. But for many U.S. industries, the major competition comes from countries such as Canada, Mexico, Brazil, South Korea, and Taiwan. And compared to the currencies of these countries, the dollar has not fallen, but has actually grown stronger. In some cases, the dollar has appreciated as much as 300% against some of those currencies in the past two years.

During the past two years (as of January 1987), the dollar's value has dropped about 45% against the Japanese yen, the Swiss franc, and the German mark. It has dropped about 35% against other European currencies, and 30% against the British pound.

Some industry and government leaders seem to believe, says Olivier, that if U.S. industry has not been saved and the trade balance improved by now, then the dollar must simply go down some more against these currencies until U.S. producers gain the upper hand. But, as she also points out, over this same two-year period, the dollar has held steady against the Canadian dollar, the Korean won, and the Hong Kong and Singapore dollars. More important, it rose 370% against the Mexican peso, 300% against the Brazilian cruzado, 100% against the Venezuelan bolivar, and 15% against the Australian dollar.

Because many U.S. industrial and agricultural products compete more against goods produced in those countries than in Japan and Europe, Olivier argues that an additional decline of the dollar against the yen or European currencies will do "absolutely nothing to help most American producers." Among those it won't help are chemical producers.

The dollar hasn't grown "weaker" for many chemicals



a Plastics and rubber. b Change in dollar's trade-weighted value from February 1985 to January 1987.
Source: Claremont Economics Institute

Mexico, Brazil help keep dollar's "value" up for chemicals

Country	Trade-weighted % change in dollar[a]					
	All chemicals	Organics	Synthetic resins	Pharmaceuticals	Inorganics	Miscellaneous chemicals
Australia	0.3%	nm	0.3%	0.5%	nm	0.7%
Belgium-Luxembourg	−1.7	−1.7%	−3.8	−1.3	−2.1%	−2.0
Brazil	8.1	12.3	6.6	nm	nm	28.6
Canada	0.1	0.1	0.1	nm	0.1	0.1
France	−2.3	−1.6	−1.8	−2.5	nm	nm
Hong Kong	nm	nm	−0.01	nm	−0.03	nm
India	nm	nm	1.2	nm	nm	nm
Italy	−1.0	−1.4	nm	−2.3	nm	nm
Japan	−4.9	−5.1	−2.8	−8.0	−4.1	−3.9
Mexico	20.0	15.1	33.6	nm	18.5	35.2
Netherlands	−2.3	−3.8	−3.0	−1.4	−4.5	−2.1
Singapore	nm	nm	nm	−0.2	nm	−0.2
South Korea	0.1	0.1	0.1	nm	0.1	nm
Spain	nm	−0.6	nm	−1.0	nm	nm
Switzerland	−0.9	−0.9	nm	−1.5	nm	nm
Taiwan	−0.2	−0.2	−0.2	nm	nm	nm
U.K.	−1.5	−2.2	−1.2	−1.7	nm	−1.3
Venezuela	nm	nm	2.2	nm	4.9	4.7
West Germany	−3.2	−3.6	−4.0	−4.3	−2.2	−2.1
TOTAL	10.5%	8.5%	27.5%	−23.7%	10.8%	57.7%

[a] Change in trade-weighted value of the dollar from February 1985 to January 1987. "Trade-weighted share" is the actual percent change in the dollar times the product's percentage share of total trade. nm = not meaningful; only data approximating 75% of each sector's total were evaluated. Source: Claremont Economics Institute

Economists generally focus on various "trade-weighted" measures of the U.S. dollar. The Federal Reserve Board index, which covers only 10 major countries, fell 39% since its early 1985 peak. Other indexes cover more countries. Generally, the more countries covered, the stronger the dollar has remained. The Dallas Federal Reserve Bank index covers 131 countries. It fell only 5%.

None of these indexes, however, tell which industries benefit, or suffer, or by how much. That is why CEI constructed a different dollar index for each specific product category. In each, the movements of the dollar against all of the various currencies are weighted by the actual proportions that each foreign country represents in that specific product trade with the U.S. In its study, CEI did not completely blanket the world, but its data cover at least 75% of U.S. trade (exports plus imports) for each product studied.

For instance, using 1985 data, Canada accounted for 15.5% of U.S. chemical trade. Japan accounted for 11.8%, and other countries each accounted for lesser shares. Applying these trade shares of each country to the dollar value change against that country's currency, CEI comes up with a trade-weighted "product-dollar" index.

For Canada, whose currency has changed little against the U.S. dollar over the past two years, the change in the "chemical-dollar" index is 0.1%. For Japan, whose yen has soared against the dollar, it is −4.9%.

By using this approach with all of the U.S.'s major chemical trading partners, CEI estimates that the U.S. chemical industry is 10.5% worse off now than it was two years ago, as far as the dollar is concerned. One reason that chemicals have not benefited much by the declining dollar is that 17.4% of U.S. chemical trade is with Canada and Australia, whose currencies have remained relatively weak against the dollar. Mexico and Brazil account for only 8% of U.S. chemical trade. But their inflation-wracked economies have made their currencies 370% and 300% weaker, respectively, against the dollar.

Earl Anderson, New York

Fine chemicals adjust to changing markets

The fine chemicals industry, to some extent, is a puzzlement: What, precisely, is meant by "fine chemicals"? To the people in the business, however, it's no puzzle. They define fine chemicals as organic compounds, made by multistep syntheses, worth more than $10 per kg. And it is, by and large, a healthy business. That's the assessment of Albert V. G. Hahn, senior adviser to Ecoplan International, Paris-based consultants, who has just completed a study on the fine chemicals industry.

The world market for fine chemicals in 1985 was about $13.8 billion, and last year it probably topped $14 billion. Nearly two thirds of that, 64%, is accounted for by pharmaceutical active compounds, and another 12% by pesticide active ingredients. Other markets, such as dye intermediates and flavors and fragrances are surprisingly small, but only because most of those compounds are priced at less than $10 per kg.

More than half the world's capacity for fine chemicals is owned by major companies—chemical producers, such as Bayer and Hoechst, and large pharmaceutical companies for captive use. These companies, many of which are European, account for 58% of capacity.

The remaining 42% of global capacity accounted for by nonmajor companies comprises as many as 400 to 450 companies. Of these, European companies account for about half of the capacity. By type of company, about half the capacity is owned by small and medium-sized pharmaceutical companies, about 30% is owned by true independent firms, and 20% by separate units or divisions, with plants dedicated to fine chemical production within large multiproduct companies, the Ecoplan report says.

The study was designed to address the strategic concerns of the fine chemicals industry. With that charter, the company was able to do some wide-ranging analysis—for example, to identify the changes sweeping through the fine chemi-

cals business. Changes are always occurring in any business sector. However, according to Ecoplan, the fine chemicals business has entered a period of major structural change, mainly as a result of changes in the primary end-use field, pharmaceuticals.

"Since 64% of fine chemical markets is pharmaceuticals, you must look at changes there," Hahn says. "And the main force behind the change in that [market] is the slowdown in the introduction of new molecules."

That is having a profound impact on pharmaceutical active-ingredient producers who heretofore have made their profits from synthesizing patented products. With fewer new, patented synthetic molecules around, fewer people can make money. Moreover, as patents expire, an increasing number of products will become generic, and it will be more difficult for small, independent companies to survive, the report predicts. For survival, a company must be big, number one in its market, and integrated, according to the report.

"Five to 10 years ago," Hahn says, "if you had suggested to any major chemical company's management that they make a molecule that wasn't theirs, they would have been aghast. They would never do such a thing.

"They looked at 'pirates'—companies that would make generic compounds, for example—with contempt. Now, they are becoming their own pirates. If it works, let's make it ourselves." Companies are more willing to market bulk products, even to their own competitors.

On the other hand, another option is to convince companies to "buy" rather than "make," or persuade them to buy advanced intermediates and leave only the final one or two steps to the formulator. The difficult steps—the hazardous or unpleasant chemistry, for example—are the early steps, and these are the domain of the fine chemicals producer.

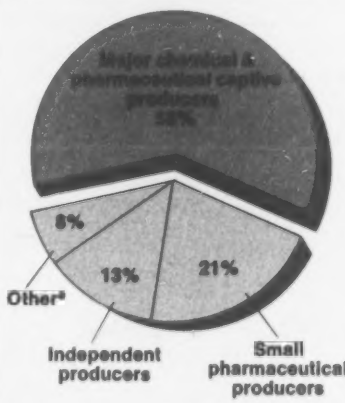
Other markets beyond pharmaceuticals are of growing interest to fine chemicals producers, too. One example is agricultural chemicals. "Until recently," Hahn says, "pesticide active ingredients were not fine chemicals, but really commodities selling for less than $10 per kg. Now, some of them, such as the pyrethroids, systemic fungicides, and new generations of low-dosage herbicides, are increasingly within the range of fine chemicals."

Similarly, fine chemicals are beginning to find their way into plastics, both as comonomers for engineering plastics and as additives or intermediates for additives, the report says. "As service temperatures or impact strength requirements rise, so do the costs of monomers and additives," Hahn notes.

Increasingly, however, producers must balance the constraints of market demand and efficient production size. Large, in the fine chemicals business, is anything more than 200,000 L of reactor capacity. "That is a big plant, and the consensus is that a good fine chemicals plant starts at that," he says. On the other hand, a limitation is imposed by market size, and physical and economic risk.

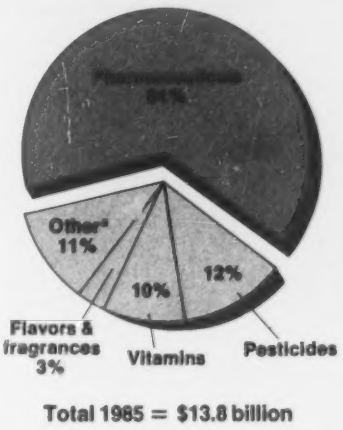
Nonetheless, the trend is toward larger reactors. Many companies have ended up with reactors that are too small. When times were easy, the small reactors were satisfactory, but as competition increased, they became less attractive economically. The result, Hahn says, is that "acquisitions are a distinct possibility, especially beyond the Alps and the Pyrenees."

Major companies own most fine chemicals capacity



a Separate units or divisions of multi-interest producers. **Source:** Ecoplan International

Pharmaceuticals take most fine chemicals demand



Total 1985 = $13.8 billion

a Includes specialty monomers and photochemicals. **Source:** Ecoplan International

Ecoplan predicts real growth of about 2.5% per year in demand to the year 2000. "Some people think there will not be so much growth per se as opportunities in make vs. buy, or doing what they do now, but better." And he adds that some producers are skeptical about even that much growth.

However, Ecoplan is reasonably confident about the prospects for the fine chemicals business. Opportunities, for example, will arise from the increasing complexity of new molecules, because whatever is easy and obvious already has been screened. More complex means more difficult reactions—but higher product prices. And growth will characterize some of the more exotic fields, such as electronic chemicals and photo initiators, although the markets are small now.

What no one seems quite sure of is the impact that biotechnology will have on the industry. "Not all that much cross-fertilization seems to be happening," Hahn observes. But there are indications that companies at least want to keep up to date on what is happening. Biotechnology is already an important processing tool for chemicals, through fermentation, as extracts or animal products, and so on. How much more important it will become remains to be seen in this already complex and challenging business.

Patricia Layman, London